



Short communication

Preparation of lithium ion conductive Al-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ thin films by a sol–gel process

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H I G H L I G H T S

- Thin films of garnet-type Al-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) were prepared by the sol–gel process.
- Coexistence of Li_2CO_3 powders is effective to suppress lithium loss during heat-treatment.
- Addition of an ionic surfactant improved the quality of the thin films.
- The ionic conductivity of the obtained thin film is $2.4 \times 10^{-6} \text{ S cm}^{-1}$ at 25 °C.

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Thin films of garnet-type Al-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) are prepared by the sol–gel process. Thin films are prepared on MgO substrates by a dip-coating process using a precursor sol from Zr-alkoxide and Li, La and Al nitrates. After the dip-coating, the dried films are calcined at 450 °C to get precursor films. When the precursor films are heat-treated at 900 °C in an alumina crucible, $\text{La}_2\text{Zr}_2\text{O}_7$ is mainly obtained. With coexistence of Li_2CO_3 powders in the crucible during the heat-treatment at 900 °C, thin film of polycrystalline cubic LLZ is obtained. Addition of an ionic surfactant, lithium dodecylsulfate, improves the quality of the thin films, and the thin film heat-treated at 900 °C with coexistence of Li_2CO_3 powders in the crucible shows the ionic conductivity of $2.4 \times 10^{-6} \text{ S cm}^{-1}$ at 25 °C.

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1. Introduction

Recently, all-solid-state thin-film lithium batteries have been recognized as micropower sources for RF-IC tags, smart cards, medical devices, microelectric mechanical systems, and so on [1]. For the fabrication of thin film batteries, physical vapor processes, such as sputtering and PVD, have been used [1–5]. However, those physical vapor processes have some disadvantages such as usage of vacuum system or difficulty in control of chemical composition and large area coating. In contrast, large area, good quality, or nano-structured and rather thick films can be prepared by the solution processes. In addition, chemical compositions of thin films can be easily controlled, and rather thick films are easily obtained in the

solution processes. Thus, solution processes like sol–gel process have been proposed to prepare thin film electrode and electrolyte materials [6–8], and the solution processes are very attractive for the development of thin film batteries.

On the other hand, all-solid-state lithium secondary batteries with inorganic solid electrolytes attract attention because of their high safety, reliability and energy density [9]. We have been developing sulfides-based electrolytes such as $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glasses and glass ceramics with high lithium ion conductivities of over $10^{-3} \text{ S cm}^{-1}$ at room temperature [9]. Compared with sulfides-based materials, lithium ion conductive oxides have rather low conductivity [10]. However, oxide materials have advantages such as their chemical stability and handling. For the application of thin film-type all solid state batteries, the thickness of the electrolyte layer is very small, and thus, oxide electrolyte with rather low lithium ion conductivity can be used as the electrolyte layer of the thin film batteries.

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Recently, garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) has been studied extensively because LLZ has high lithium ion conductivity ($\sigma_{\text{total}} > 10^{-4} \text{ S cm}^{-1}$ at room temperature) in cubic phase and chemical stability against lithium metal [11–14]. Although the bulk conductivity is close to $10^{-3} \text{ S cm}^{-1}$, a very high temperature is needed for the sintering to reduce grain boundary resistance. To obtain a dense cubic LLZ, a heat-treatment at around 1200°C is required in the conventional solid state reaction method. Such a heat-treatment at high temperatures causes a lithium loss from LLZ. In addition, for the preparation of thin films, a reaction between substrates or electrode materials and the electrolyte, during the heat-treatment at high temperatures, is serious problem. Thus, a low temperature process to prepare LLZ thin films is desired. Sol-gel process has been used for the low-temperature synthesis of LLZ powders [15–19], and we have also reported that the composite with sol-gel derived Al-doped LLZ and Li_3BO_3 shows the room temperature lithium ion conductivity of about $1 \times 10^{-4} \text{ S cm}^{-1}$ with the heat treatment at 900°C [20,21]. About LLZ thin films, preparation of LLZ thin films by using the pulsed laser deposition has only been reported [22,23].

In the present study, thin films of garnet-type Al-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) were successfully prepared by the sol-gel process. Thin films were prepared on MgO substrates by a dip-coating process using a precursor sol from Zr-alkoxide and Li, La and Al nitrates. The precursor films were heat-treated at 900°C in an alumina crucible with coexistence of Li_2CO_3 powders to avoid lithium loss during heat-treatment. In addition, an ionic surfactant, lithium dodecylsulfate (LDS), was added to the precursor sol for the improvement of the surface morphology of the thin films.

2. Experimental

Firstly, LiNO_3 and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 1-propanol. Separately, $\text{Zr}(\text{O}-n\text{-C}_3\text{H}_7)_4$ and $\text{Al}(\text{O}-\text{sec-C}_4\text{H}_9)_3$ were mixed with Ethylacetoacetate (EAcAc) in 1-propanol. These two solutions were mixed, and the obtained solution was stirred at room temperature

for 12 h. The mole ratio of LiNO_3 : $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$: $\text{Zr}(\text{O}-n\text{-C}_3\text{H}_7)_4$: $\text{Al}(\text{O}-\text{sec-C}_4\text{H}_9)_3$: EAcAc: 1-propanol is 7.7:3.0:2.0:0.3:4.0:50. When LDS was used, 0.1 wt% of LDS was added to the coating solution, and the solution was additionally stirred for 1 h. Thin films were prepared by a dip coating process on MgO substrate. The obtained precursor thin films were calcined at 450°C for 15 min. The thin films were further heat-treated at 900°C in an alumina crucible with coexistence of Li_2CO_3 powders. To avoid the reaction between MgO substrate and LLZ thin films, the heat-treatment temperature was limited to be 900°C . Au-sputtered MgO substrates can also be used at a heat-treatment at 900°C , but other substrates such as Al_2O_3 , Pt, and $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ cannot be used because of the reactions with LLZ thin films.

X-ray diffraction (XRD) patterns were obtained by X-ray diffractometer (XRD-6000, Shimadzu). A scanning electron microscope (SEM) (JSM-6610A, JEOL) was used for the observation of the morphology of thin films.

Compositional depth profiling of the samples was obtained using a TOF-SIMS 5 spectrometer (IonTof). A pulsed 25 keV Bi^+ primary ion source was employed for analysis, delivering 1.2 pA of target current over a $20.8 \mu\text{m} \times 20.8 \mu\text{m}$ area. Sputtering was done using a 1 keV oxygen beam over a $250 \mu\text{m} \times 250 \mu\text{m}$ area. Data acquisition and post-processing analyses were performed using the Ion-Spec software.

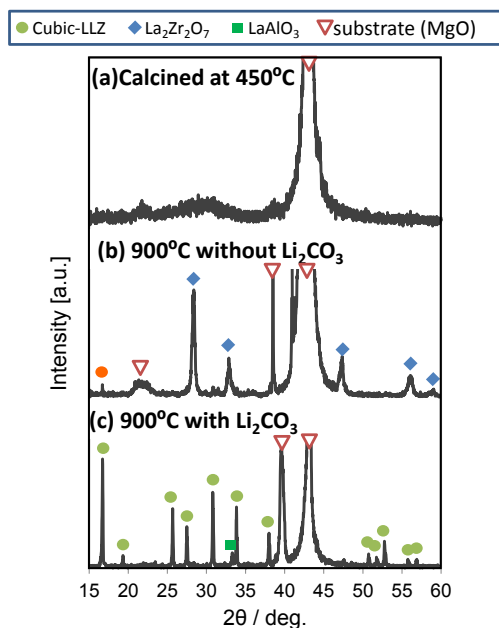


Fig. 1. XRD patterns of (a) the precursor thin film calcined at 450°C , (b) heat-treated thin film at 900°C without Li_2CO_3 , and (c) heat-treated thin film with Li_2CO_3 powders.

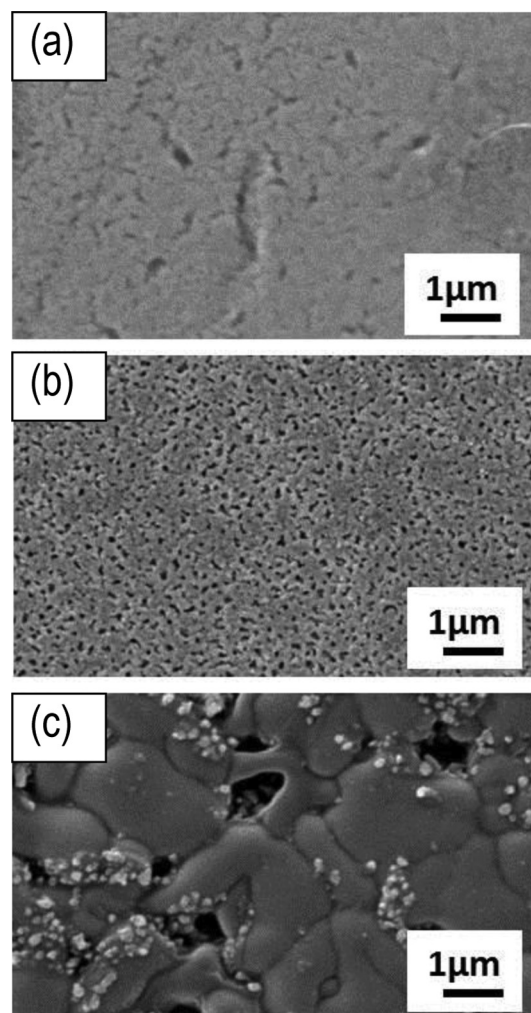


Fig. 2. SEM images of Al-doped LLZ thin films (a) calcined at 450°C , (b) heat-treated at 900°C without Li_2CO_3 , and (c) heat-treated at 900°C with Li_2CO_3 powders.

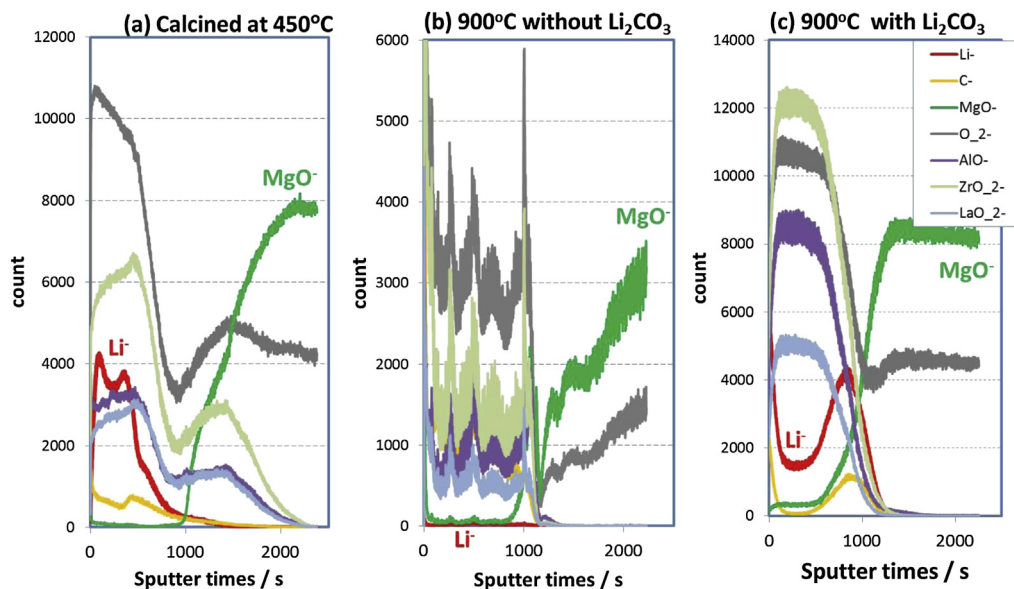


Fig. 3. Depth composition analysis determined by TOF-SIMS for Al-doped LLZ thin films (a) calcined at 450 °C, (b) heat-treated at 900 °C without Li₂CO₃, and (c) heat-treated at 900 °C with Li₂CO₃ powders.

AC impedance was measured by an impedance analyzer (SI 1260; Solartron) in frequency range 0.1 Hz–1 MHz. Gold electrodes were sputtered on the surface of the thin films.

3. Results and discussion

Fig. 1 shows the XRD patterns of (a) the precursor thin film calcined at 450 °C, and (b) heat-treated thin films at 900 °C without Li₂CO₃ and (c) heat-treated thin films at 900 °C with Li₂CO₃ powders. The thickness of the films was about 1 μm, determined by the SEM observation. The precursor thin film calcined at 450 °C was amorphous. When the precursor films were heat-treated at 900 °C in an alumina crucible without Li₂CO₃, La₂Zr₂O₇ was mainly obtained. However, with coexistence of Li₂CO₃ powders in the crucible during heat-treatment at 900 °C, thin film of polycrystalline cubic LLZ with very small amounts of LaAlO₄ was obtained. This suggests that lithium loss during the heat-treatment is suppressed by the coexistence of Li₂CO₃ powders in the crucible.

Fig. 2 shows surface SEM images of Al-doped LLZ thin films (a) calcined at 450 °C, (b) heat-treated at 900 °C without Li₂CO₃, and (c) heat-treated at 900 °C with Li₂CO₃ powders. The surface was dense after the calcination. However, many pores were observed on the film heat-treated at 900 °C without Li₂CO₃. Growth of large

grains was observed on the surface of the thin film heat-treated at 900 °C with Li₂CO₃ powders.

Fig. 3 shows depth composition analysis determined by TOF-SIMS for Al-doped LLZ thin films (a) calcined at 450 °C, (b) heat-treated at 900 °C without Li₂CO₃, and (c) heat-treated at 900 °C with Li₂CO₃ powders. Here, the results are discussed by focusing on lithium concentration. In the calcined sample (a), signal from lithium proves a homogeneous distribution of Li in the film. In the thin film heat-treated at 900 °C without Li₂CO₃, almost no signal from Li was observed. This is in accordance with XRD results, where La₂Zr₂O₇ was mainly observed. In the film heat-treated at 900 °C with Li₂CO₃ powders, a homogeneous distribution of Li was observed. These results suggest that lithium was lost during the heat-treatment at 900 °C, and the coexistence of Li₂CO₃ powders in the crucible is very effective to suppress the loss of lithium during the heat-treatment at 900 °C.

Because the surface of the film heat-treated at 900 °C with Li₂CO₃ powders showed very large grains with rather large surface roughness, an ionic surfactant containing lithium (LDS) was added to the coating solution to improve the surface morphology of the films. Fig. 4 shows surface SEM image of Al-doped LLZ thin films heat-treated at 900 °C with Li₂CO₃ and (a) without LDS and (b) with LDS. It was found that the addition of the ionic surfactant improved

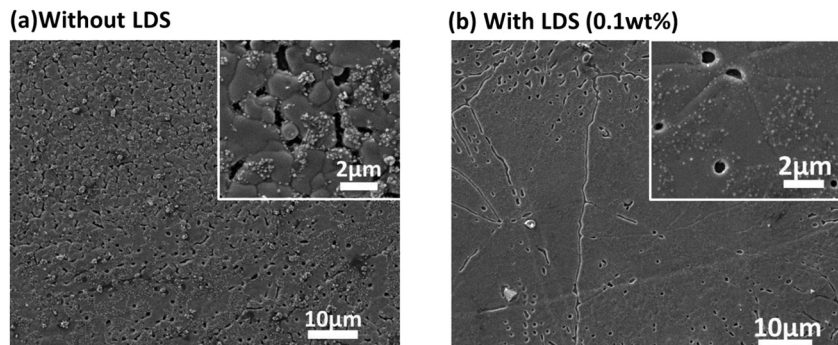


Fig. 4. SEM image of Al-doped LLZ thin films heat-treated at 900 °C with Li₂CO₃ and (a) without LDS and (b) with LDS.

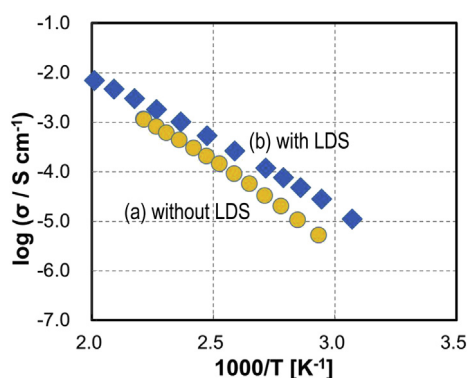


Fig. 5. The Arrhenius plots of the ionic conductivity for the Al-doped LLZ thin films heat-treated at 900 °C with Li_2CO_3 and (a) without LDS and (b) with LDS.

the morphology of the thin films: very dense microstructure was observed in the thin film with LDS.

Fig. 5 shows the Arrhenius plots of the ionic conductivity for the Al-doped LLZ thin films heat-treated at 900 °C with Li_2CO_3 and (a) without LDS and (b) with LDS. From the Arrhenius plots of the ionic conductivity, the total electrical conductivity at room temperature and activation energy for conduction of the Al-doped LLZ thin films without LDS was calculated to be $2.8 \times 10^{-7} \text{ S cm}^{-1}$ and 59 kJ mol^{-1} , respectively, and by the addition with LDS, the total electrical conductivity at room temperature and activation energy for conduction was improved to be $2.4 \times 10^{-6} \text{ S cm}^{-1}$ and 50 kJ mol^{-1} , respectively. Although the ionic conductivity of the thin film ($2.4 \times 10^{-6} \text{ S cm}^{-1}$) is rather low than that of bulk Al-doped LLZ, the conductivity is comparable to that of LiPON thin films. Thin film samples may show higher conductivity with much higher heat-treatment temperatures. However, a heat-treatment at higher temperatures than 900 °C must cause the reaction between the substrate and electrolyte, and also the loss of lithium during heat-treatment, and thus, the samples heat-treated at higher temperatures than 900 °C were not examined. In the preparation of bulk pellet samples, mother powders are often used to suppress the lithium loss during sintering. However, for the thin film samples, removal of mother powders from the surface of thin films is very difficult without the damage of thin film surface. Therefore, we have proposed the heat-treatment of a thin film in a crucible with coexistence of Li_2CO_3 powders, in the present study. This process is proved to be very effective for suppressing lithium loss during heat-treatment. Thus, it can be applicable to a heat-treatment of thin films deposited with other techniques.

4. Conclusions

Thin films of garnet-type Al-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) were prepared by the sol–gel process. When the precursor films were heat-treated at 900 °C in an alumina crucible, $\text{La}_2\text{Zr}_2\text{O}_7$ was mainly obtained. With coexistence of Li_2CO_3 powders in the crucible during the heat-treatment at 900 °C, thin film of polycrystalline cubic

LLZ was obtained. The heat-treatment process of a thin film in a crucible with coexistence of Li_2CO_3 powders is proved to be very effective for suppressing lithium loss during heat-treatment. Addition of an ionic surfactant, lithium dodecylsulfate, improved the quality of the thin films, and thin films heat-treated at 900 °C with coexistence of Li_2CO_3 powders in the crucible showed the ionic conductivity of $2.4 \times 10^{-6} \text{ S cm}^{-1}$ at 25 °C.

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